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Evidence for K-rich terranes on Vesta from impact spherules

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Abstract—The howardite-eucrite-diogenite (HED) clan is a group of meteorites that probably originate from the asteroid Vesta. Some of them are complex breccias that contain impact glasses whose compositions mirror that of their source regions. Some K-rich impact glasses (up to 2 wt% K_2O) suggest that in addition to basalts and ultramafic cumulates, K-rich rocks are exposed on Vesta's surface. One K-rich glass (up to 6 wt% K_2O), with a felsic composition, provides the first evidence of highly differentiated K-rich rocks on a large asteroid. They can be compared to the rare lunar granites and suggest that magmas generated in a large asteroid are more diverse than previously thought.

INTRODUCTION

The early stages of planetary formation in the solar system involved a large population of small to medium-sized objects, colliding with each other to form the major planets (Weidenschilling 2000). Some of them melted and differentiated into a metallic core, an ultramafic mantle, and a basaltic crust. Most of these primitive differentiated bodies have now disappeared, such that the formation and degree of differentiation of these primitive small and medium-sized planets is still a matter of debate (McCoy et al. 2006). Today, only a handful of such small planets are still orbiting in the asteroid belt, between Mars and Jupiter (Sunshine et al. 2004). Vesta, one of them, is differentiated with an intact internal structure, and is covered by basalts and pyroxenites. It is probably the source of one of the most important group of differentiated meteorites, namely the howardite, eucrite, and diogenite (HED) suite (e.g., Drake 2001). Eucrites are basaltic rocks that display magmatic textures indicating formation as lava flows or intrusions. Diogenites are orthopyroxene-rich cumulates that formed in a plutonic environment. Diogenites and eucrites are often breccias consisting of a mixture of crystal debris and rock fragments reflecting many impact events on the surface of their parent body. Howardites are more complex breccias made chiefly of eucritic and diogenitic clasts. They occasionally contain impact melt clasts, glass beads or debris (e.g., Noonan 1974). Some of these glasses could have been ballistically transported from distant impact sites and mixed to the regolith before the impact responsible for the launch of the meteorites from the parent body. Thus, these glasses may originate from terrains not directly sampled by typical HED meteorites, and could therefore provide, in addition to future remote sensing observations, a complementary view of the composition of the surface of Vesta.

Here, we report on the petrography and the major element geochemistry of impact spherules and glass fragments from seven howardites. We will show that some of the glasses cannot be explained by impact melting of typical HED lithologies. Some K-rich impact glasses (up to 2 wt% K_2O) suggest that in addition to basalts and ultramafic cumulates, K-rich rocks are exposed on Vesta.

ANALYTICAL METHODS

We determined the major-element compositions of the glasses by electron microprobe analysis using a Cameca Camebax at Hawai'i Institute of Planetology, Honolulu (Bununu and Kapoeta), a JEOL JXA8200 at National Institute of Polar Research, Tokyo (Yamato [Y-] 7308 and 791208), and a Cameca SX100 at Ifremer, Plouzané (LaPaz Icefield [LAP] 04838, Northwest Africa [NWA] 1664 and 1769). All analyses used wavelength dispersive spectrometers at 15 KV accelerating voltage, 10–12 nA beam current, and a spot size ranging from 10 to 30 μm. In the case of phases in the porphyritic glasses (NWA 1664, NWA 1769 and LAP 04838), and for the felsic area in a NWA 1664 spherule, 1 μm spots

were used. Minerals (wollastonite [Si, Ca], orthoclase [K], albite [Na], apatite [P]), oxide ($MnTiO_3$ [Mn, Ti]), Al_2O_3 [Al], Fe_2O_3 [Fe], Cr_2O_3 [Cr], FeS_2 [S], etc.), and metal standards (Ni) were used for calibration. In order to avoid the heterogeneity effects induced by small crystals or inclusions, the compositions of the glasses given here are averages of 2 to 30 analyses depending of the size of the object. Analyses of inclusions or rims of the spherules have been excluded from the averages.

Raman spectra were acquired with a Labram HR800 model of Jobin-Yvon Horiba spectrometer equipped with a microscope for collection of backscattered Raman signal and equipped with a CCD detector. The spectrometer was used in backscattering geometry. The laser beam (514.5 nm exciting lines of a Spectra Physics® Ar^+ laser) was focused through microscope objectives (×100) down to a 1 micrometer spot on sample and the backscattered light was collected through the same objective.

RESULTS

Seven glass-bearing howardites (Bununu, Kapoeta, LAP 04838, NWA 1664 and 1769, Y-7308 and Y-791208) have been selected. In all the samples, glassy objects are heterogeneously dispersed in a fine-grained clastic matrix, together with diogenitic and eucritic fragments. They generally consist of spherules (or beads) and more frequently angular fragments.

Petrography

Spherules

Spherules are generally ellipsoidal in shape, and commonly about 500 μm in diameter (Figs. 1 and 2). They are often broken. A variety of textures are revealed by scanning electron microscopy. Some are fully glassy (Fig. 1 A and B), while others are vitrophyric containing olivine or pyroxene crystals in a glassy matrix. The morphologies of the crystals are similar to those obtained experimentally in fast cooled basaltic or ultramafic melts (e.g., Donaldson et al. 1975; Arndt et al. 1984; Faure et al. 2003). Three types of olivine morphology occur in the spherules: lattice olivine (Fig. 1C), fiber olivine (Fig. 2A), and chains of skeletal crystals (Figs. 2C, 3, and 4). Dendritic (Fig. 4A) pyroxenes are common. The variety of crystal shapes are clearly related to cooling rate and degree of undercooling of the melts (e.g., Donaldson et al. 1975; Arndt et al. 1984; Faure et al. 2003) and not surprisingly, point to very fast cooling rate values (in the order of a few K/s or faster). Furthermore, droplets or grains of metal (typically Fe 98 wt%, Ni 2 wt%) and troilite are present in most of the spherules, and are normally less than 30 μm in diameter. Detailed chemical mapping performed on selected spherules shows that some of them are coated by minute grains of sulfides and phosphates that are unfortunately too small to be properly analyzed by electron microprobe (Fig. 5). Similar coatings have been previously described on impact spherules from the Moon, and are interpreted as condensates from a vapor cloud formed with the spherules (Ruzicka et al. 2000). Furthermore, the spherules are not always chemically uniform. In addition to possible small scale heterogeneities in the melts, which can be strongly obscured by the development of dendritic crystals, some of the spherules have rims nearly devoid of Na and K (Na_2O and K_2O < 0.02 wt%, see Fig. 5), which suggests that they have lost a significant portion of their alkalis during their flight and cooling.

Three unusual spherules were analyzed during the course of this study. The first one, found in NWA 1769 (Fig. 6), displays an orthopyroxene nucleus coated with an homogeneous glass that contains rare tiny Ca-rich plagioclase grains. The orthopyroxene crystal is unzoned, and has a typically diogenitic composition ($En_{74.6}Wo_{2.2}Fs_{23.2}$, FeO/MnO = 30, see Table 1). This would appear to be a remnant of the target, which has melted to form the glass. The second one is a broken spherule found in NWA 1664 (Figs. 3 and 4). This object displays a vitrophyric texture with chains of skeletal olivine and dendritic clinopyroxene crystals. Interestingly, this fragment is a composite, as it consists of three different types of glassy areas (Table 1), all cross-cut by the olivine crystals. The fragment is dominated by a Na-poor, K-rich glass (Mg# [=100 × Mg/(Mg + Fe), atomic)] = 53.1, Na_2O = 0.20 wt%, K_2O = 1.41 wt%), mostly in the internal part of the spherule. The external rim of the spherule is Na-rich and K-poor (Mg# = 47.0, Na_2O = 1.21 wt%, K_2O = 0.06 wt%). Finally, a felsic glass is located in a 15 μm thick strip (red in the K map; Fig. 3). The glassy nature of the felsic component is confirmed by Raman spectra (Fig. 7). A few K rich patches are seen in the core of the broken spherule (Fig. 3) and correspond either to interstitial glass areas enriched in K after the crystallization of olivine and pyroxene, or areas slightly contaminated by the felsic melt. These K-rich patches should not be overemphasized, and their scarcity confirms that the different melts did not mix together significantly inside the spherule. Furthermore, the limits between the felsic and the mafic glasses are sharp, and indicate that the melts involved were largely immiscible. The last one, found again in NWA 1664 (#1664B7,2S) contains two different mafic glasses, both K-rich (Table 1 and Fig. 8). Again, the boundaries between the two different glasses are sharp.

Fragments of Glass

Angular fragments of glass, sometimes vesicular, are more frequent than spherules (Figs. 9 and 10). They are generally small (typically a few hundreds of μm), but some as large as 2 cm have been previously reported in NWA 1664 (Kurat et al. 2003). They can be fully glassy, vitrophyric, to crystal-rich, and many display textures very similar to those of the spherules. Crystal-rich glasses display a wide range of

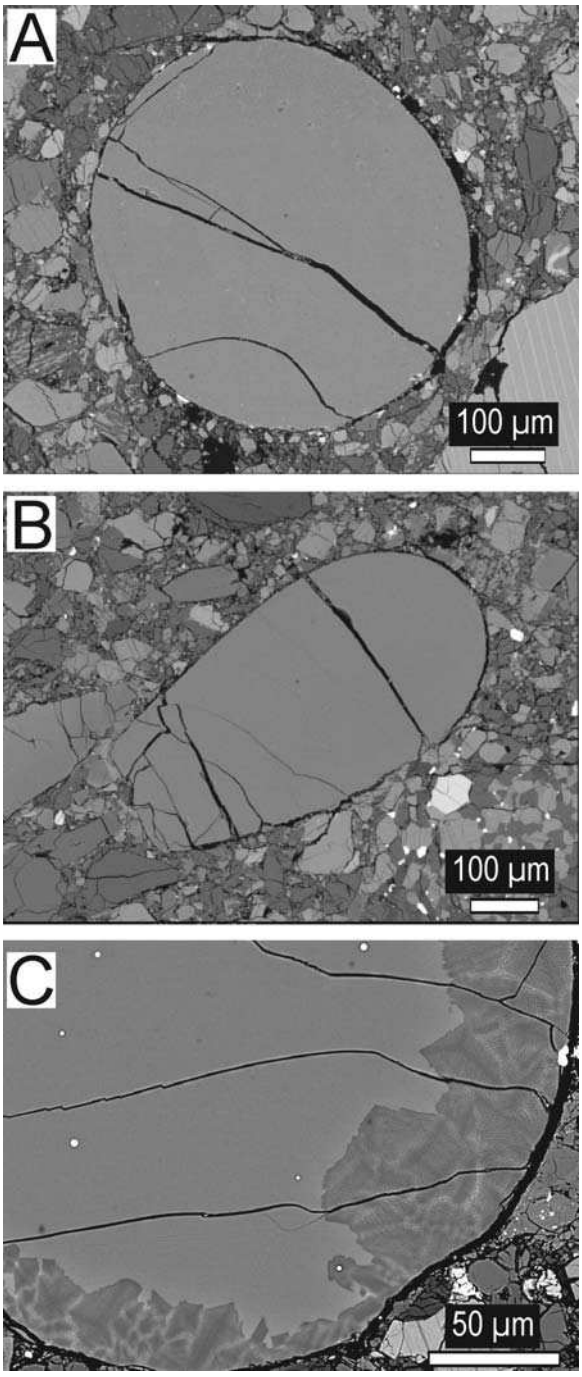

Fig. 1. Backscattered electron images of glass spherules from howardites. A and B) Vitreous spherules from NWA 1769. C) Vitreous spherule from Y-7308 with lattice olivine in its rim. Notice the droplets of metal (white).

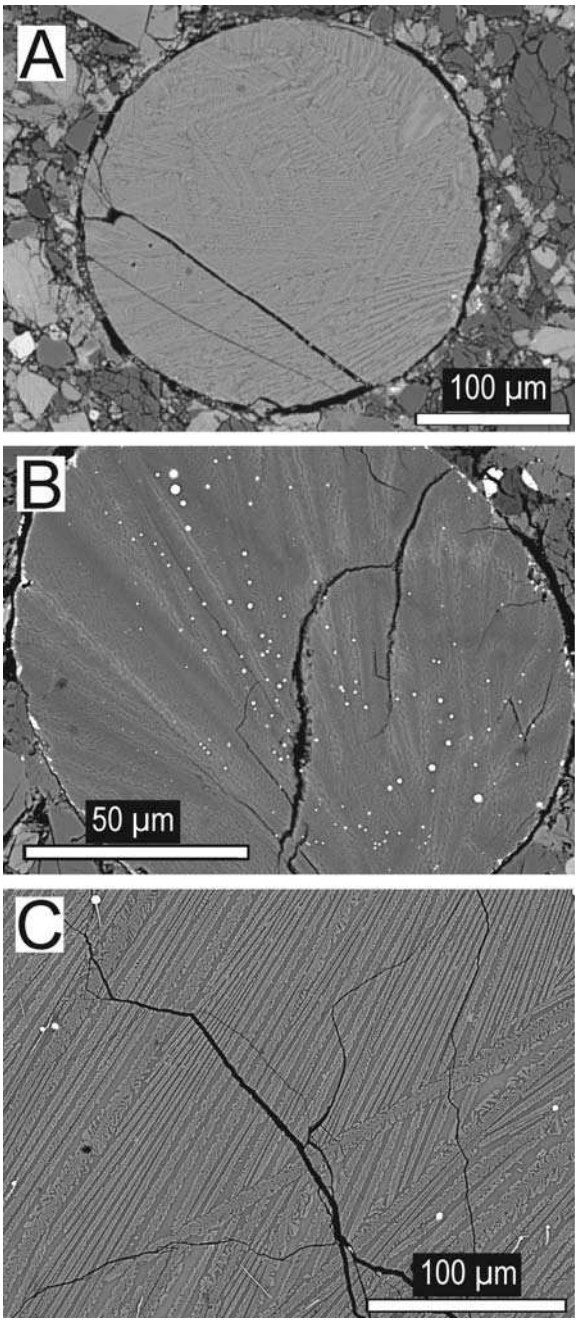

Fig. 2. Backscattered electron images of glass spherules from howardites. A) Spherule from NWA 1769 with fibre and lattice olivine. B) Spherule from Y-7308 with radiating olivine chains and pyroxene crystals (?). Notice the droplets of metal (white). C) Quenched-texture in a spherule from Y-7308.

features. Here we provide only a short description of two of them which display different mineral assemblages.

The first one occurs in NWA 1664 (clast 1664B3, 3). This clast contains low-Ca pyroxene and olivine phenocrysts in glass (Fig. 10B, and Table 1). Minor phases are metal ($Fe_{98}Ni_2$) and troilite. The pyroxene crystals are unlike typical diogenitic pyroxenes (e.g., Fowler et al. 1994; Mittlefehldt 1994). They are zoned from $En_{80.1}Wo_{2.1}Fs_{17.8}$ in the cores to $En_{69.0}Wo_{6.6}Fs_{24.4}$ in the rims, and are Al and Cr-rich (Al_2O_3 = 1.5–4.0 wt%, Cr_2O_3 = 0.95–2.1 wt%). Such unusual concentrations have been previously measured in pyroxenes from fast cooled lunar basalts and impactites (Engelhardt et al. 1989; Barrat et al. 2003). Olivine crystals are unzoned (Fo_{64}).

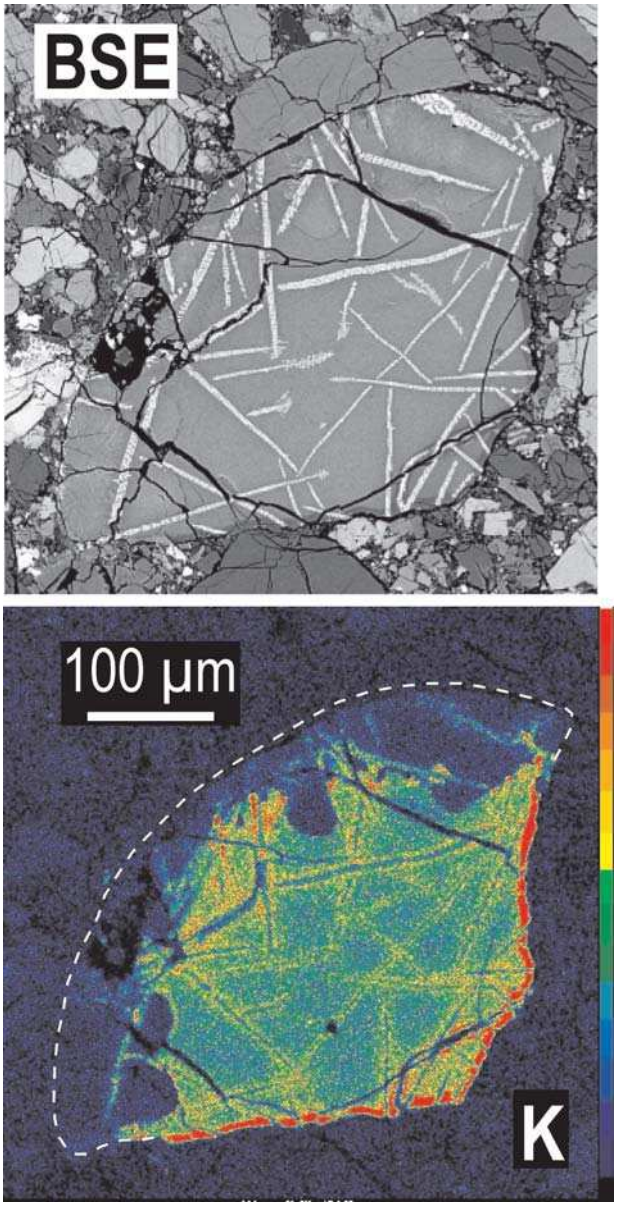

Fig. 3. Backscattered electron image and K map of the broken impact spherule found in NWA 1664 that contains a felsic glass. The shape of the felsic area before the fragmentation of the spherule is unknown. This glass is located in a 15 µm thick strip (red in the K map) in contact with a Na-poor, K-rich mafic glass (Mg# = 53.1, Na_2O = 0.20 wt%, K_2O = 1.41 wt%) that composes apparently the internal part of the spherule. Chains of skeletal olivine crosscut the boundaries between the different glasses.

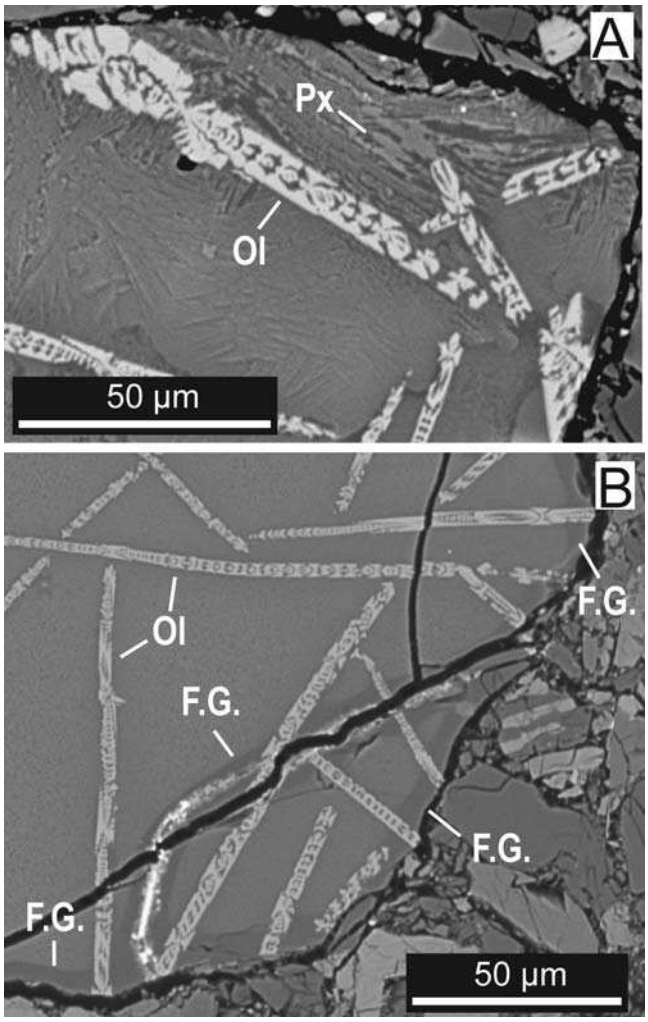

Fig. 4. Backscattered electron images of the broken impact spherule found in NWA 1664 that contains a felsic glass. A) Chains of skeletal olivine crystals (Ol) and dendritic pyroxene (px). B) Chains of skeletal olivine (Ol) crosscut the strip of felsic glass (dark grey, F.G.).

The second clast is from LAP 04838 (clast LAP, 2). The glass contains two types of crystals (Fig. 10C and Table 1). The first, most abundant, type consists of plagioclase and equilibrated pyroxene debris which are clearly derived from a eucritic precursor. These angular fragments do not have the morphology of unmelted remnants sometimes found in impact melts (shock features are missing here). Thus, they are more likely regolith-derived and enclosed by the melt at a late stage. The second consists of pyroxenes (50 µm in length), sometimes skeletal, which have grown from the glass. These crystals are strongly zoned from low-Ca cores ($En_{63}Wo_7Fs_{30}$) to pigeonitic rims ($En_{32}Wo_{29}Fs_{39}$), with again a strong Al enrichment (Al_2O_3 from 4 to 11.8 wt%).

Chemistry

Because it is not always possible to accurately reverse-calculate the composition of the original melt represented by the crystal-rich glass fragments, we have restricted our study to the spherules and aphyric glass fragments. Sixty-one glassy clasts or spherules have been analyzed here (Table 1), and their average compositions are compared to howardites, eucrites and diogenites in Fig. 11. Three chemically different types of glasses have been recognized:

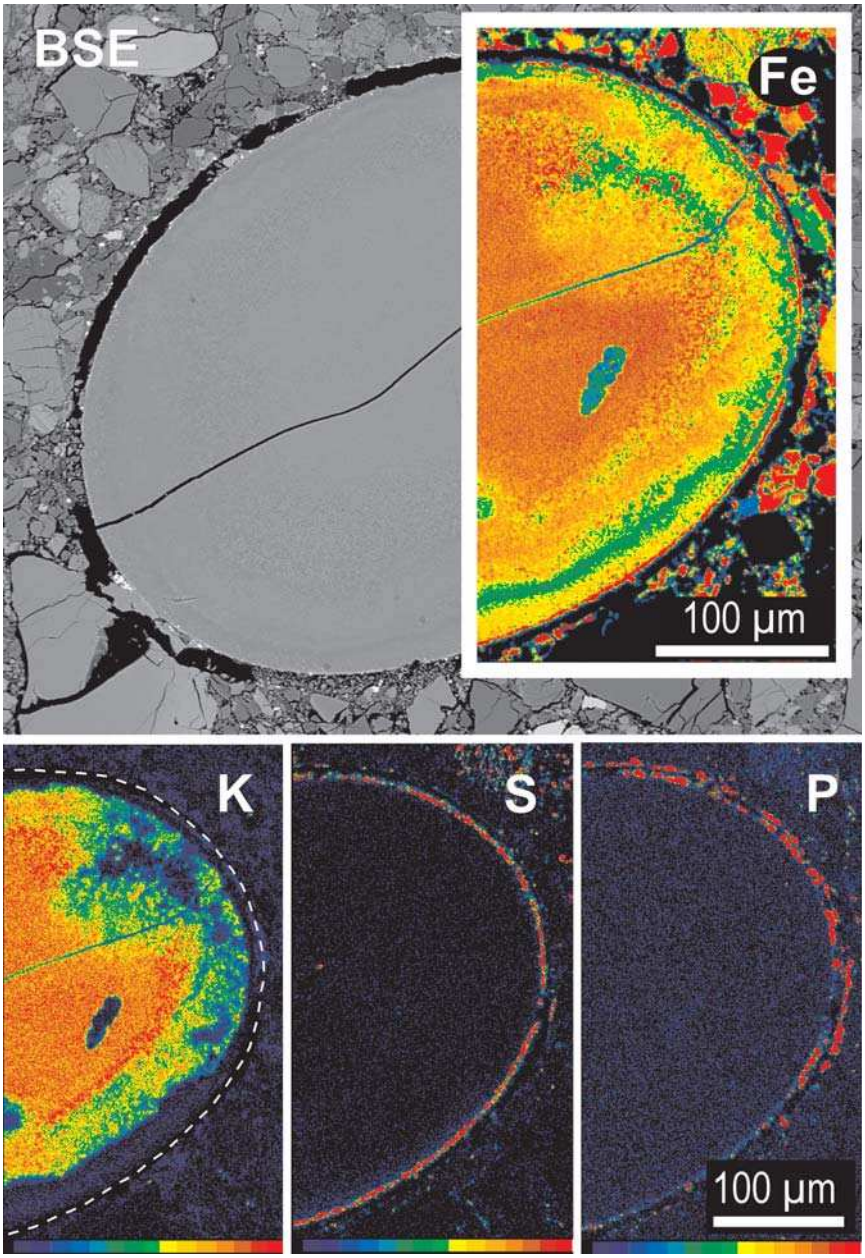

Fig. 5. Backscattered electron image and maps of Fe, K, S, and P of an heterogeneous spherule found in NWA 1769 that contains a rim devoid of K and a coating made of fine sulfide and phosphate grains.

1. Glasses from Bununu, Kapoeta, Y-7308, and Y-791208, including data from Noonan (1974), Yagi et al. (1978), Klein and Hewins (1979), Noonan et al. (1980), Delaney et al. (1982), and Ikeda and Takeda (1984), display a wide range of composition with Mg# from 41 to 72, which overlap those of eucrites and howardites. These glasses are K-poor, with K_2O generally less than 0.1 wt%.
2. Mafic glasses found in NWA 1664, NWA 1769, and LAP 04838 display a range of compositions similar to the previous K-poor glasses, with Mg# from 32 to 73, although in some cases they have significantly lower Ca and Na than expected for typical HED lithologies. More importantly, they are unusually K-rich, with K_2O concentrations ranging from 0.17 to 2.33 wt%. High-K abundances were previously noticed in glasses from NWA 1664 (Kurat et al. 2003), Luotolax (Delaney et al. 1982) and from the Malvern howardites (Noonan 1974; Desnoyers and Jérome 1977). These K abundances are much higher than those reported for most of the HED meteorites, which contain in most cases less than 0.1 wt% K_2O.

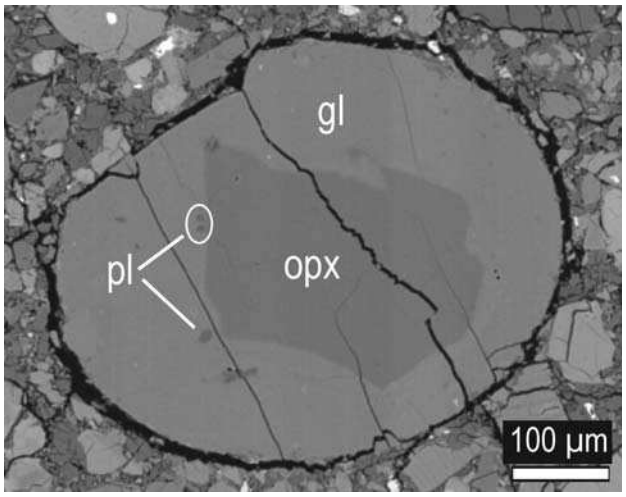

Fig. 6. Backscattered electron images of a composite impact spherule found in NWA 1769 with an orthopyroxene nucleus (opx). The glass (gl) contains small plagioclase grains (pl).

3. The silica-rich glass found in a fragment of a spherule from NWA 1664, displays high K_2O abundances ranging from 4 to 6.12 wt%. The compositions correspond to a high-K, low Na monzogranite. CIPW norms indicate a small excess of Al_2O_3 (normative corundum from 0.8 to 2.91%), which could be the result of a loss of alkalis during impact.

DISCUSSION

Glasses found in howardites can be produced by two different processes, either volcanic fire-fountaining (Delaney et al. 1982) or impact melting. We agree with previous studies that a volcanic origin is unlikely, and these glasses, including the K-rich ones, have certainly formed upon impacts from lithologies exposed on 4 Vesta (e.g., Noonan 1974; Hewins and Klein 1978; Yagi et al. 1978; Klein and Hewins 1979; Noonan et al. 1980; Ikeda and Takeda 1984; Boesenberg et al. 2007): schlieren (e.g., Kurat et al. 2003), and meteoritic Fe-Ni metal have been often observed in spherules and glassy fragments. In addition, the occurrence of a remnant of a diogenitic orthopyroxene in the core of a spherule strengthens this interpretation.

The occurrence of composite spherules containing different types of glasses (spherules 1664B1,1S and 1664B7,2S) could suggest at first glance that silicate liquid immiscibility (SLI) played a role during their formation. However, we do not favor the involvement of such a process during the cooling of the spherules for at least three reasons:

1. If SLI was operative, composite spherules should be relatively common; instead, such objects are more the exception than the rule.
2. Experimental works have shown that pairs of liquids generated by SLI exhibit contrasting chemical compositions (Thompson et al. 2007); the chemical differences between the mafic glasses found in the spherules #1664B1,1S and #1664B7,2S (Table 1) are much less marked.
3. Although silica-rich melts similar to the felsic glass found in spherule #1664B1,1S can be produced by SLI, and are associated with low-Si, high Fe melts (Powell et al. 1980), their compositions are unlike the mafic melts found in the same spherule.

We suggest that the different glasses found in the rare composite spherules are more likely the remnants of heterogeneities in the target. Thus, as lunar impact glasses or terrestrial impactites and tektites, the compositions of the glasses found in howardites can provide strong constraints on the nature of their source regions.

The abundances of the least volatile elements straddle the fields drawn by the HED meteorites (Fig. 11, e.g., Al_2O_3, CaO and TiO_2 versus FeO/MgO). It can be emphasized that the range of the FeO/MnO ratios shown by the glasses and the HED meteorites are similar. Among the 61 mafic clasts and spherules we have analyzed during the course of the study, only 2 display values significantly different from the HED ones (1769A, 2S and 4S, see Table 1). The possible contamination of the glasses by metal from the impactor, or more likely the occurrence of an unusual lithology in the target (see below) can perfectly explain these outliers. However, the high K concentrations observed in impact glasses from NWA 1664 and NWA 1769 howardites, are astonishing.

Although hot-desert alteration can affect the composition of meteorites significantly, K abundances in the glassy clasts and spherules are certainly pristine. No K enrichment was detected close to the fractures or to the surface of both NWA 1664 and NWA 1769 howardites. The glassy objects were the only places where high K abundances were observed. The fusion crusts of both meteorites exhibit very low K concentrations, ruling out the possibility of a selective contamination of glasses. Furthermore, high K concentrations have been measured in glasses from the LAP 04838 howardite, a find from Antarctica, and more importantly, from the Luotolax and Malvern howardites (Noonan 1974; Desnoyers and Jérome 1977; Delaney et al. 1982), and from the Macibini polymict eucrite (Buchanan et al. 2000), which are observed falls, and consequently have not suffered terrestrial weathering.

Clearly, the high-K concentrations displayed by some impact spherules require the contribution of an unusual component either from the impactor or the impacted area. The first hypothesis is unlikely because many of the impact glasses studied here contain much more K than all known meteorites. Therefore, their high-K concentrations are either linked to the compositions of the molten lithologies or generated by the shock processes. Potassium enrichments

Table 1. Averaged compositions of individual glassy fragments and spherules in howardites. Values are in wt%.

#	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total	Mg#	FeO/MnO
Kapoeta, spherules (S) or glassy fragments (F)														
BR3, S	50.36	0.43	9.13	0.67	18.32	0.51	14.21	7.25	0.36	0.03	0.04	101.31	58.02	35.92
K1-DB, S	50.42	0.56	11.10	0.50	18.25	0.48	10.71	8.77	0.21	0.16	0.01	101.17	51.13	38.02
C29, F	50.96	0.47	9.91	0.65	17.54	0.49	13.72	7.39	0.31	0.04	0.05	101.53	58.23	35.80
C1, F	48.19	0.63	11.54	0.25	20.87	0.62	9.23	9.32	0.19	0.01	0.09	100.94	44.08	33.66
C16, F	50.65	0.37	6.88	0.66	18.17	0.50	16.56	6.46	0.23	0.01	0.04	100.53	61.90	36.34
BR17, F	49.86	0.42	13.25	0.47	16.13	0.48	10.30	9.53	0.27	0.02	0.03	100.76	53.22	33.60
DC21, F	51.57	0.35	6.70	0.65	17.47	0.52	17.83	5.66	0.22	0.01	0.01	100.99	64.54	33.60
DC43, F	50.77	0.38	8.82	0.69	16.79	0.49	16.36	6.69	0.20	0.03	0.01	101.23	63.45	34.27
Bununu, spherules (S) or glassy fragments (F)														
B1, S	50.73	0.39	8.58	0.63	17.47	0.52	14.81	6.92	0.25	0.03	0.02	100.35	60.18	33.60
B2, S	50.83	0.44	8.91	0.61	17.46	0.59	14.43	7.13	0.25	0.04	0.04	100.73	59.57	29.59
B3, F	49.73	0.74	12.58	0.26	18.84	0.62	7.42	10.86	0.39	0.08	0.05	101.57	41.25	30.39
B4, F	48.91	0.64	12.69	0.22	16.81	0.53	8.72	12.24	0.31	0.05	0.06	101.18	48.03	31.72
B5, F	51.00	0.52	13.74	0.47	15.36	0.53	8.73	10.20	0.34	0.03	0.04	100.96	50.34	28.98
B6, F	50.78	0.53	9.96	0.52	17.69	0.53	12.59	7.93	0.32	0.05	0.04	100.94	55.92	33.38
Y-7308, spherules (S) or glassy fragments (F)														
85-2, 1 F	51.81	0.22	6.00	1.01	16.12	0.50	19.62	4.72	0.06	0.01		100.07	68.45	32.24
85-2, 2 F	52.47	0.18	4.80	1.16	15.77	0.51	21.49	3.61	0.04	0.12		100.15	70.84	30.92
85-3, 1 S	51.04	0.26	6.03	0.92	16.23	0.51	19.30	4.86	0.13	0.01		99.29	67.93	31.82
85-4, 1 F	52.35	0.17	4.40	1.21	15.58	0.50	21.90	3.49	0.07	0.12		99.79	71.47	31.16
104-2, 1 S	53.83	0.21	4.50	1.24	15.04	0.56	20.70	3.68	0.13	0.08		99.97	71.04	26.86
104-2, 2 F	52.17	0.22	5.97	1.01	15.33	0.54	19.61	4.70	0.14	0.17		99.86	69.51	28.39
104-3, 1 S	51.60	0.22	5.88	1.03	16.18	0.52	19.74	4.64	0.12	0.07		100.00	68.50	31.12
Y-791208, glassy fragment (F)														
81-2, 1 F	49.52	0.27	6.71	0.93	17.33	0.53	19.12	5.21	0.16	0.02		99.80	66.29	32.70
NWA 1664, fusion crust, spherules (S) or glassy fragment (F)														
1664P, fusion crust	48.54	0.58	10.58	0.40	17.59	0.53	10.66	8.70	0.37	0.02	0.03	98.00	51.92	33.19
1664P, 1 S	48.19	0.60	11.01	0.47	19.36	0.66	10.61	8.81	0.09	0.75	0.02	100.57	49.41	29.33
1664P, 2 S	48.84	0.97	9.92	0.58	19.60	0.64	10.89	7.82	0.10	0.84	0.02	100.22	49.76	30.63
1664P, 3 S	51.83	0.33	8.96	0.45	15.04	0.47	16.39	5.80	0.10	0.76	0.01	100.14	66.00	32.00
1664P, 4 F	49.84	0.50	11.98	0.49	14.48	0.48	12.21	9.74	0.21	0.25	0.07	100.25	60.05	30.17
1664P, 5 F	48.69	0.86	12.48	0.28	19.82	0.60	6.04	11.12	0.25	0.35	0.10	100.59	35.22	33.03
1664B1, 1 F	49.68	0.58	11.78	0.44	17.74	0.53	9.23	9.97	0.21	0.44	0.04	100.64	48.11	33.47
1664B1, 2 F	49.96	0.64	11.99	0.43	17.20	0.53	8.77	9.02	0.15	1.31	0.05	100.05	47.62	32.45
1664B1, 3 F	49.15	1.19	12.89	0.23	19.12	0.54	5.19	11.32	0.30	0.68	0.11	100.72	32.63	35.41
1664B1, 4 F	49.79	0.79	12.71	0.31	18.71	0.57	6.39	10.63	0.27	0.41	0.11	100.69	37.85	32.82
1664B1, 5 F	49.11	0.57	12.03	0.53	16.15	0.55	10.55	8.98	0.16	1.07	0.04	99.74	53.80	29.36
1664B2, 1 F	49.30	0.78	12.68	0.36	17.94	0.56	7.15	10.78	0.23	0.58	0.06	100.42	41.53	32.04
1664B2, 2 F	49.00	0.73	12.06	0.38	17.89	0.56	7.45	9.40	0.18	1.46	0.07	99.18	42.60	31.95
1664B3, 1 S	47.04	0.52	9.64	0.55	19.68	0.70	13.25	8.04	0.04	0.18	0.05	99.69	54.55	28.11
1664B3, 2 S	51.20	0.61	9.91	0.23	19.24	0.65	8.02	8.61	0.24	0.68	0.10	99.49	42.63	29.60
1664B4, 1 S	49.08	0.62	10.54	0.39	18.94	0.64	9.57	8.68	0.15	0.77	0.07	99.45	47.40	29.74
1664B4, 2 S	49.11	0.58	10.03	0.39	19.29	0.66	10.28	8.44	0.14	0.54	0.07	99.53	48.72	29.12
1664B5,1S	49.55	0.54	9.82	0.57	18.33	0.62	11.75	7.25	0.09	0.93	0.04	99.50	53.32	29.69
1664B5,2S	48.84	0.65	11.94	0.42	18.26	0.61	8.93	9.30	0.18	0.78	0.04	99.96	46.57	29.71
1664B5,3S	48.43	0.57	9.70	0.60	17.74	0.55	13.18	8.41	0.08	0.46	0.01	99.72	56.98	32.32

Table 1. *Continued.* Averaged compositions of individual glassy fragments and spherules in howardites. Values are in wt%.

#	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total	Mg#	FeO/MnO
1664B6,1S	53.57	0.40	10.10	0.47	11.46	0.40	16.89	6.18	0.14	1.06	0.01	100.68	72.43	28.65
NWA 1664, crystal-rich glass (1664B3, 3)														
Glass	49.85	0.53	14.86	0.39	12.68	0.47	7.74	11.77	0.31	0.65	0.05	99.30	52.09	27.04
Opx (core)	54.75	0.12	1.57	0.95	11.50	0.54	28.96	1.05	0.00	0.00	0.01	99.45	81.78	21.32
Opx (rim)	51.24	0.19	4.03	2.11	14.58	0.68	23.19	3.10	0.01	0.01	0.01	99.15	73.93	21.36
Ol (core)	36.36	0.04	0.01	0.02	31.62	0.65	31.47	0.08	0.00	0.00	0.02	100.27	63.95	48.97
Ol (rim)	36.56	0.02	0.04	0.08	31.20	0.62	31.40	0.06	0.00	0.04	0.02	100.04	64.20	50.54
NWA 1664, composite spherule (1664B1,1S)														
Mafic glasses														
1664B1, 1 S, core	51.10	0.73	13.38	0.45	13.17	0.47	8.34	10.91	0.20	1.41	0.01	100.17	53.04	28.02
1664B1, 1 S, rim	49.82	0.72	13.17	0.43	15.52	0.54	7.72	10.82	1.21	0.06	0.07	100.08	47.00	28.74
Felsic glass														
High K (n=11)	66.41	1.04	17.87	0.26	1.97	0.08	0.21	4.99	0.56	5.80	0.01	99.20	16.07	24.63
Low K (n=2)	65.36	1.11	18.96	0.49	1.96	0.05	0.19	7.04	0.61	3.95	0.00	99.72	14.58	39.20
NWA 1664, composite spherule (1664B7,2S)														
Glass 1	48.83	0.64	12.30	0.49	17.30	0.51	9.20	10.48	0.25	0.37	0.05	100.42	48.66	34.16
Glass 2	49.78	0.65	12.19	0.51	17.07	0.57	9.36	9.06	0.16	1.32	0.08	100.76	49.42	29.91
NWA 1769, fusion crust, spherules (S) or glassy fragments (F)														
1769A, fusion crust	49.06	0.54	10.47	0.36	18.69	0.57	10.34	8.74	0.34	0.03	0.04	99.18	49.65	32.79
1769A, 1 S	48.27	0.63	10.81	0.44	18.80	0.55	11.63	8.90	0.14	0.28	0.01	100.46	52.43	34.18
1769A, 2 S	48.45	0.46	7.71	0.69	22.50	0.41	15.43	2.12	0.22	2.33	0.02	100.34	55.01	54.88
1769A, 3 S	49.42	0.50	8.44	0.69	17.20	0.54	16.03	6.65	0.05	0.37	0.01	99.90	62.42	31.85
1769A, 4 S	45.89	0.63	10.39	0.49	23.09	0.53	11.84	4.89	0.29	1.79	0.01	99.84	47.75	43.57
1769A, 5 S	49.83	0.55	9.24	0.57	16.36	0.61	13.11	8.67	0.10	0.65	0.03	99.72	58.81	26.82
1769A, 6 S	50.51	0.67	12.01	0.41	15.79	0.55	8.45	9.48	0.20	1.48	0.01	99.56	48.82	28.71
1769A, 8S	49.44	0.91	12.10	0.35	19.77	0.64	5.95	10.41	0.27	0.60	0.02	100.46	34.92	31.07
1769B, 1 S	49.22	0.58	11.25	0.48	17.69	0.61	10.00	8.80	0.14	1.10	0.04	99.91	50.19	29.00
1769B, 2 S	49.88	0.59	11.01	0.49	17.00	0.58	10.50	8.73	0.14	0.92	0.01	99.85	52.39	29.31
1769B, 3 S	49.52	0.57	10.80	0.29	21.34	0.55	8.72	6.05	0.26	1.83	0.00	99.93	42.13	38.80
1769B, 4 F	50.61	0.61	11.74	0.49	16.83	0.53	10.56	8.47	0.29	0.17	0.03	100.33	52.80	31.75
1769B, 5 F	49.35	0.88	12.21	0.31	19.42	0.59	6.14	10.57	0.25	0.70	0.04	100.46	36.03	32.92
1769C, 1 S	49.94	0.56	9.53	0.62	17.03	0.66	12.99	7.25	0.11	0.78	0.01	99.48	57.61	25.80
NWA 1769, spherule with an orthopyroxene nucleus (1769C, 2S)														
Glass	49.62	0.62	11.72	0.54	16.75	0.61	9.53	9.14	0.16	1.21	0.05	99.95	50.35	27.46
Opx	54.68	0.06	0.73	0.61	15.02	0.50	27.13	1.14	0.01	0.00	0.02	99.90	76.30	30.25
LAP 04838, glass fragment														
LAP, 1 F	49.21	0.85	11.19	0.41	18.26	0.60	8.33	9.95	0.18	0.72	0.09	99.79	44.84	30.33
LAP 04838, crystal-rich glass fragment														
LAP, 2 F	48.44	0.96	11.63	0.37	18.99	0.66	7.18	10.20	0.43	0.50	0.09	99.45	40.26	28.75
Opx1 (core)	50.82	0.45	3.88	1.26	17.86	0.62	21.49	3.53	0.02	0.01	0.01	99.95	68.20	28.61
Opx2 (core)	50.46	0.40	4.08	1.38	18.59	0.64	21.31	3.03	0.03	0.00	0.00	99.92	67.15	29.10
Opx2 (rim)	49.00	0.91	11.80	0.34	17.19	0.61	7.75	10.01	0.60	0.37	0.06	98.64	44.57	28.20
Pl	46.04	0.03	33.28	0.00	0.40	0.06	0.04	17.27	1.68	0.07	0.01	98.88		
Px (low Ca)	50.18	0.37	0.57	0.29	30.98	0.94	15.20	1.40	0.02	0.00	0.00	99.95	46.66	32.85
Px (high Ca)	48.81	0.92	2.42	1.10	14.56	0.51	12.03	17.92	0.17	0.00	0.02	98.46	59.56	28.72

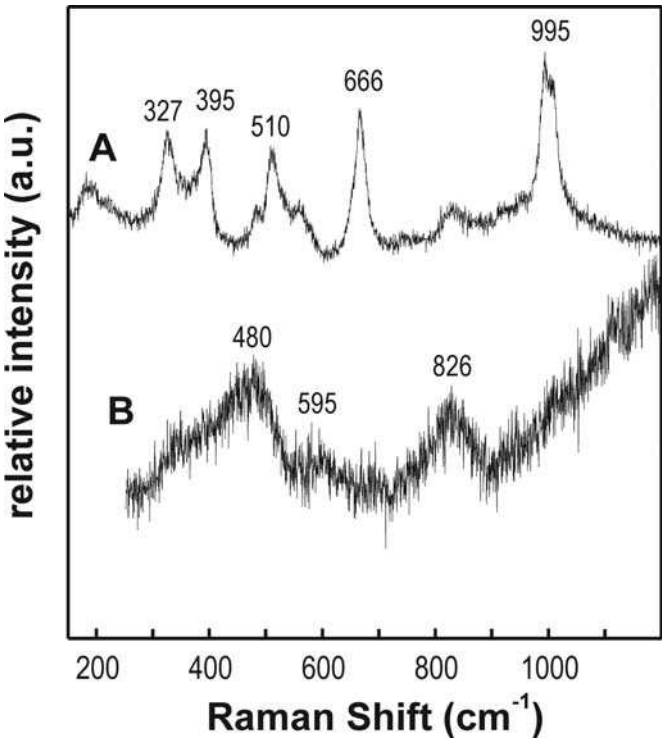

Fig. 7. Raman spectra recorded on two locations of the broken impact spherule shown in Figs. 3 and 4. Spectrum A has been obtained in the mafic glass poor in Na and enriched in K. The bands are characteristic of clinopyroxene. The spectrum bears also features of a silicate glass confirming the intermix of glass and crystallites. Spectrum B has been recorded in the felsic glass forming the K-rich strip. The spectrum is that of a pure glass with no trace of crystalline phases. The broad bands are characteristic of silica-rich glass.

have been occasionally observed in terrestrial impactites, and were ascribed to the contribution of alkali-rich liquids or seawater (Grieve 1978). Such an explanation is, of course, not applicable to the case of a dry body such as Vesta. Alternatively, impactites can be enriched in K via volatilization/condensation processes during crater formation (Yakovlev and Parfenova 1980). The latter mechanism could be operative on Vesta, and would result in selective enrichments and losses of elements depending on differences in their volatilization and condensation temperatures. However, it is not clear that such processes can account for a large K enrichment in impacted lithologies (one or two orders of magnitude in order to explain the compositions of the K-rich glasses). On the Moon, where rocks have suffered the effects of many impact events in a dry and airless environment like Vesta, Si-, Na-, K-, P-, and S-rich condensates have been observed in soils, but are generally small (<400 nm) and scarce (Keller and McKay 1992). Among the thousands of lunar impact glasses that have been analyzed so far, only a few display K_2O abundances up to 1 wt%. In these cases, K-rich condensates are not required to explain the high K concentrations, which can be better rationalized by the involvement of K-rich lithologies, KREEP or less commonly granites (Lindstrom et al. 1991; Zellner et al. 2002; Zeigler et al. 2006). Alternatively, a K-enrichment in impact glasses is possible if the target is only partially melted, and if K is concentrated in the most fusible fraction. Such a process explains the composition of the glasses found in the so-called agglutinates (aggregates found in the lunar regolith, that consist of mineral, lithic and glass fragments cemented together by a glass and interpreted as impact-fused soil). They display generally enrichments in Al, Ca, Na, and K, and depletions in Mg, Fe, Mn in comparison to the bulk soil composition (e.g., Papike et al. 1982; Taylor et al. 2001). Indeed, the chemical compositions of the agglutinitic glasses approach the bulk composition of the finer fractions of the soils, which are enriched in the most friable (and fusible) components, namely feldspar and mesostasis. It is now accepted that agglutinitic glasses formed chiefly from the fusion of these finest fractions (F^3 model, Papike et al. 1981; Basu et al. 2002). Their enrichments in Ca, Na, and K are linked to the composition of the feldspar fraction, and the latter is not particularly K-rich. Thus, the K abundances in agglutinitic glasses are generally low (K_2O <0.5 wt%, e.g., Papike et al. 1982; Taylor et al. 2001 and references therein). Although the F^3 model could be effective on Vesta, such a process cannot account for the high-K abundances measured in glasses during the course of the study. The feldspar grains found in howardites are essentially eucritic plagioclases. Like the feldspars found in lunar soils, they are Ca-rich, in the range of bytownite to anorthite and have low K concentrations. Thus, if this process was operative on Vesta, it would have produced glasses with a range of K abundances similar to the lunar agglutinate one. Moreover, impact spherules and glass fragments are certainly not produced by the same processes as agglutinates. Hence, we will not further consider this possibility.

The compositions of the glasses found in the howardites have been plotted in a K_2O/CaO versus Al_2O_3/CaO plot (Fig. 12), and this diagram has important implications. Al and Ca are both refractory elements (e.g., Delano et al. 1981). Consequently, the Al_2O_3/CaO will not be significantly fractionated by impact melting. On the other hand, the K_2O/CaO ratio is highly sensitive to possible loss of K during melting, or enrichment in K via volatilization/condensation processes. A selective K-enrichment would result in an erratic behavior of K, and in a decoupling of K with respect to refractory elements, such as Fe, Al, or Ca (Delano et al. 1981). A very good correlation is obtained for the NWA 1664 and NWA 1769 glasses in the K_2O/CaO versus Al_2O_3/CaO plot. This relationship rules out condensation processes and strongly suggests the presence of K-rich components in their source region (Fig. 12). This conclusion is strengthened by the occurrence of the unmixed felsic melt in a spherule whose composition can potentially explain part of the scattering of

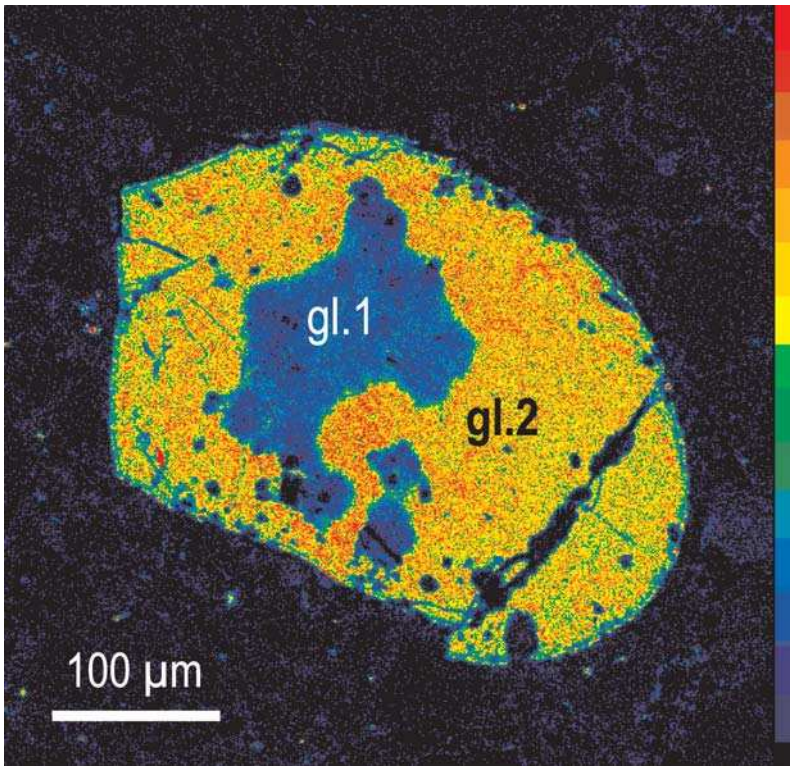

Fig. 8. K map of an impact spherule found in NWA 1664 (#1664B7,2S) that contains two basic K-rich glasses (K_2O = 0.37 and 1.32 wt% for glass 1 and glass 2, respectively).

the data outside of the generally accepted HED field (Figs. 11 and 12).

Glasses are the only K-rich components present in the NWA 1664 and NWA 1769 howardites. Thus, unlike the low-K impact spherules found in the Bununu, Kapoeta, and Yamato howardites, the NWA 1664 and NWA 1769 glasses could not have formed by the melting of a source similar to their host breccias, nor from any combination of the known HED meteorites. Because of their high-K abundances, they necessarily originate from terranes not sampled, or not yet recognized, in HED meteorites.

The proportions of the different lithologies that were involved during the genesis of the impact melts can be estimated with mixing calculations, but are highly dependent on the chosen endmember compositions (Koeberl 2007). In order to estimate the proportions of the main eucritic and diogenitic lithologies involved during the genesis of the impact glasses found in howardites, we have performed mixing calculations using the Mona program (Metzner and Grimmeisen 1990). Usui and McSween (2007) have shown that combinations of three endmembers, namely, a diogenite (e.g., Shalka), a cumulate eucrite (e.g., Serra de Magé), and a low-Mg eucrite (e.g., Nuevo Laredo), reproduce all the major element abundances of HED meteorites satisfactorily (Usui and McSween 2007). Therefore, we have selected these endmembers for our calculations. Very good fits are obtained in the case of low-K impact glasses, indicating that impact induced vapor fractionation effects, if any, are negligible. Examples of fits are given in Table 2, and the results are plotted in a ternary plot and compared with howardites (Fig. 13).

In the case of the high-K spherules, the K_2O/CaO and FeO/CaO versus Al_2O_3/CaO plots infer the involvement of one or more additional components significantly outside the chemical field of the HED (Fig. 12). A felsic endmember with the composition of the felsic glass found in a NWA 1664 can partly account for the high-K abundances of the spherules but not for the high FeO/CaO ratios shown by some of them. We have tentatively performed a series of least square calculations using a variety of HED lithologies and the felsic melt found in NWA 1664, but unfortunately no conclusive results have been obtained, suggesting that the selected endmembers were inappropriate. Better estimations of the proportions of the different lithologies involved during the genesis of the glasses must await new discoveries of high-K lithologies in HED meteorites.

A question of major importance concerns the origin or source of the felsic glass found in a NWA 1664 spherule fragment. One may argue that it formed from a fragment of mesostasis from a eucrite. This is unlikely because these mesostases do not show high-K concentrations, and K-feldspar has been observed in one case only (Barrat et al. 2007). The felsic glass is more likely an impact glass formed

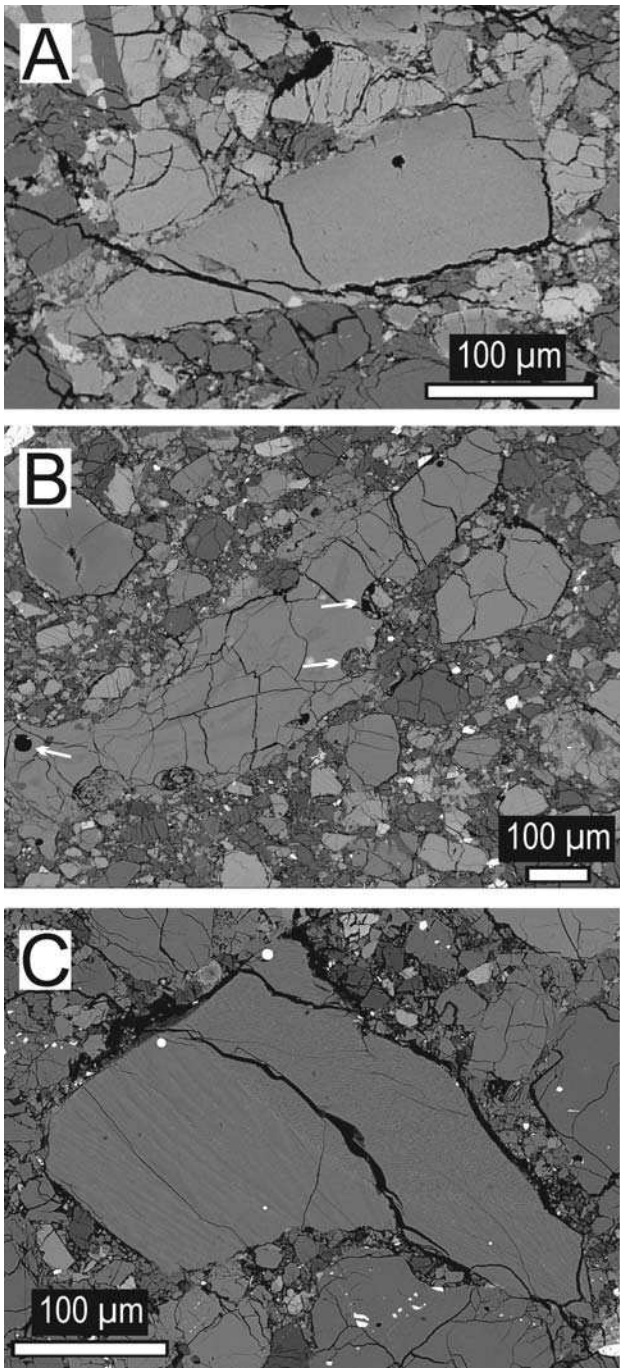

Fig. 9. Backscattered electron images of glass fragments from howardites. A) Vitreous fragment from LAP 04838. B) Vesicular glass fragment from NWA 1664. C) Glassy fragment from Y-7308 with very fine olivine and pyroxene crystals.

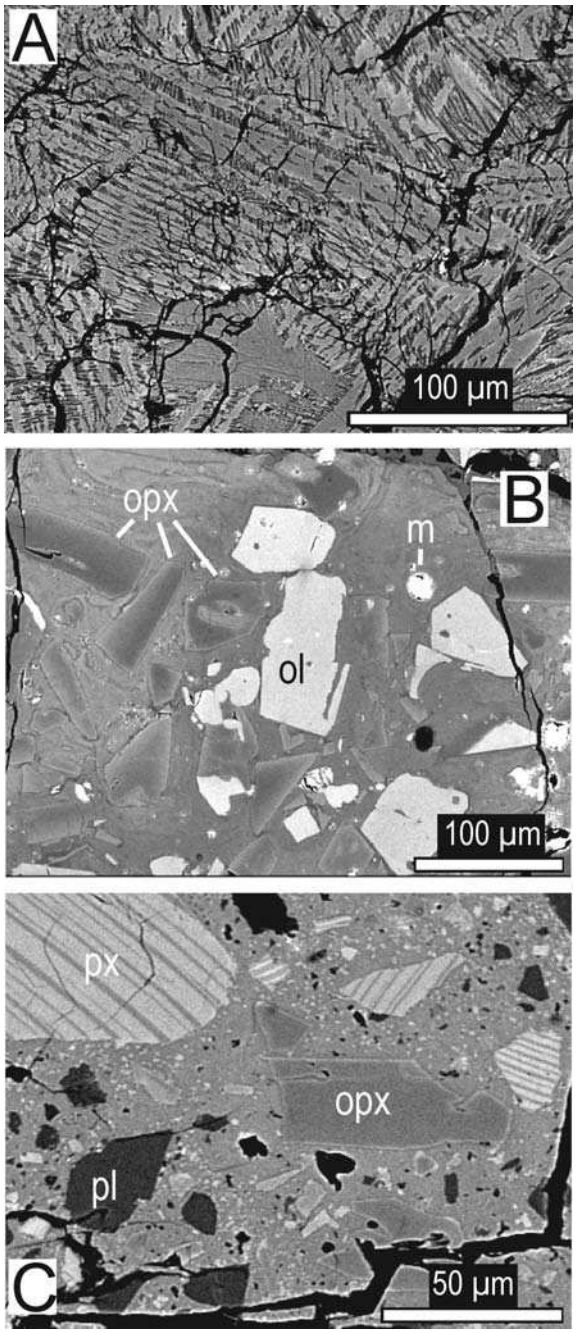

Fig. 10. Backscattered electron images of glass fragments from howardites. A) Skeletal pyroxene crystals in a glassy fragment from LAP 04838. B) Crystal-rich fragment from NWA 1664 (ol: olivine, opx: low-Ca pyroxene, m: metal). C) Crystal rich fragment from LAP 04838 (px: equilibrated eucritic pyroxene, pl: plagioclase, opx: low-Ca pyroxene).

at the expense of a K-rich granitic or felsic clast present in the Vesta regolith. Interestingly, a small felsic glass with a much lower K_2O abundance (1 wt% only) was previously described in a diogenitic breccia (Takeda 1986), and confirms that acidic melts have been generated by the magmatic activity on Vesta.

Direct evidence of extraterrestrial rocks resembling granites is exceedingly rare. For example, rare iron meteorites display some inclusions that contain K-feldspar or K-rich glasses (e.g., Mittlefehldt et al. [1998]; Ruzicka et al. [2006]). Four small granitic clasts have been found in some LL chondritic breccias (Bischoff et al. [1993]; King

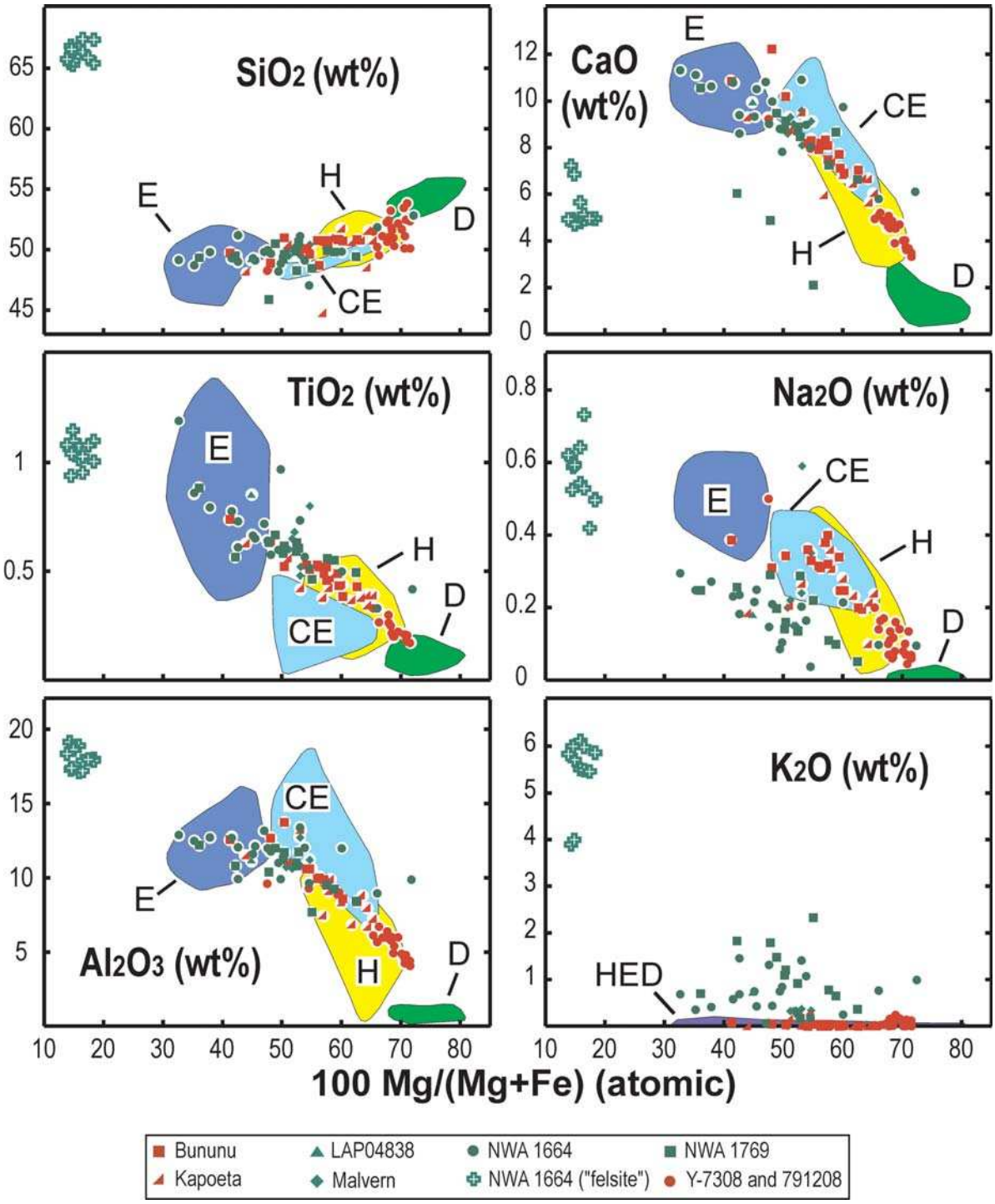

Fig. 11. SiO_2, TiO_2, Al_2O_3, CaO, Na_2O, and K_2O (wt%) versus 100 × Mg/(Mg + Fe) (atomic) plots for impact glasses from howardites (Noonan [1974]; Desnoyers and Jérome [1977]; Yagi et al. [1978]; Hewins and Klein [1978]; Klein and Hewins [1979]; Noonan et al. [1980]; Delaney et al. [1982]; Ikeda and Takeda [1984], and this study). The fields for eucrites (E), cumulate eucrites (CE), diogenites (D), and howardites (H) are drawn from a compilation of literature data (see references in Mittlefehldt et al. [1998] and Barrat et al. [2007, 2008]).

et al. [2005]; Sokol et al. [2007]). The other known extraterrestrial granites were collected on the Moon during the Apollo missions (Papike et al. 1998). All lunar granites analyzed so far are very small fragments (the largest weighs only 1.7 g) characterized by high SiO_2 (60 to 74 wt%) and K_2O (2 to 10.4 wt%), and low Na_2O (0.4 to 1.9 wt%) (Papike et al. 1998). Interestingly, the NWA 1664 glass resembles the lunar samples, but exhibits much higher

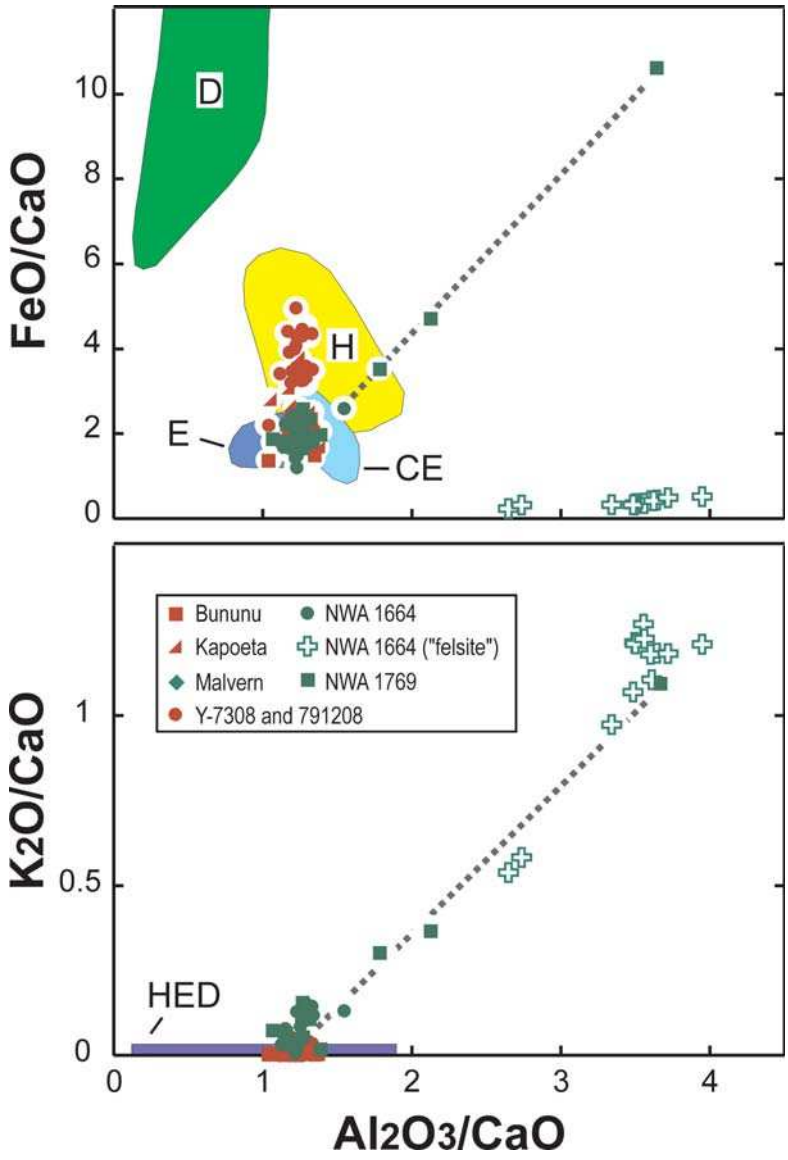

Fig. 12. FeO/CaO, and K_2O/CaO versus Al_2O_3/CaO (wt%/wt%) plots for impact glasses from howardites (Noonan [1974], Desnoyers and Jérome [1977]; Yagi et al. [1978]; Hewins and Klein [1978]; Klein and Hewins [1979]; Noonan et al. [1980]; Delaney et al. [1982]; Ikeda and Takeda [1984], and this study). The fields for eucrites (E), cumulate eucrites (CE), diogenites (D), and howardites are drawn from a compilation of literature data (see references in Mittlefehldt et al. [1998] and Barrat et al. [2007, 2008]). The dotted line is the trend defined by the K-rich spherules.

Al_2O_3 abundances (about 18 wt% compared to 8.8–13 wt% in the lunar granites).

The rare lunar granites demonstrate that felsic melts can be generated on a dry planetary body, but their origin is still the subject of debate. It has been proposed that these melts result from extreme magma differentiation involving silicate liquid immiscibility (Papike et al. 1998). If this process was operative on the Moon, it could also be on Vesta. Indeed, extreme crystallization of a eucritic melt has been experimentally performed, and a K-rich felsic melt generated by silicate liquid immiscibility was obtained (Powell et al. 1980). Alternatively, remelting of the crust produced by basaltic underplating could have generated felsic or granitic magmas on the Moon (Hagerty et al. 2006). On Vesta, remelting of the crust could have certainly occurred but was unable to generate directly K-rich acidic melts (Barrat et al. 2007).

CONCLUSIONS

The K-rich impact glasses found in howardites suggest that the magmatic activity, which built Vesta's crust, was particularly complex. It is almost certain that the rocks that outcrop on this body are not restricted to mafic cumulates and

Table 2. Comparison of average glass compositions (this study) with those obtained from the mixing calculations using the given endmembers (oxides in wt%). The proportions of endmembers are given in wt%.

SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Endmembers									
Shalka									
53.15	0.06	0.62	1.44	16.79	0.57	26.57	0.75	0.04	0.00
Nuevo Laredo									
48.59	0.92	12.16	0.30	20.56	0.62	5.61	10.72	0.47	0.06
Serra de Magé									
48.64	0.13	14.84	0.63	14.44	0.48	10.73	9.83	0.25	0.01
Mixing calculations									
Bununu (average, n = 6)									
49.88	0.54	10.98	0.45	17.12	0.55	11.02	9.13	0.31	0.04
Model (16.51 % Shalka + 42.91% Nuevo Laredo + 41.16 Serra de Magé)									
49.65	*0.46*	*11.43*	*0.63*	*17.54*	*0.56*	*11.21*	*8.77*	*0.31*	*0.03*
Kapoeta (average, n = 8)									
49.84	0.45	9.57	0.56	17.76	0.50	13.47	7.55	0.25	0.04
Model (29.79% Shalka + 40.95 Nuevo Laredo + 29.21 Serra de Magé)									
49.94	*0.43*	*9.50*	*0.74*	*17.64*	*0.56*	*13.35*	*7.48*	*0.28*	*0.03*
Y-7308 (average, n = 7)									
52.25	0.21	5.38	1.08	15.77	0.52	20.37	4.25	0.10	0.08
Model (63.69 Shalka + 3.67 Nuevo Laredo + 33.45 Serra de Magé)									
51.90	*0.12*	*5.81*	*1.14*	*16.28*	*0.54*	*20.72*	*4.16*	*0.13*	*0.01*

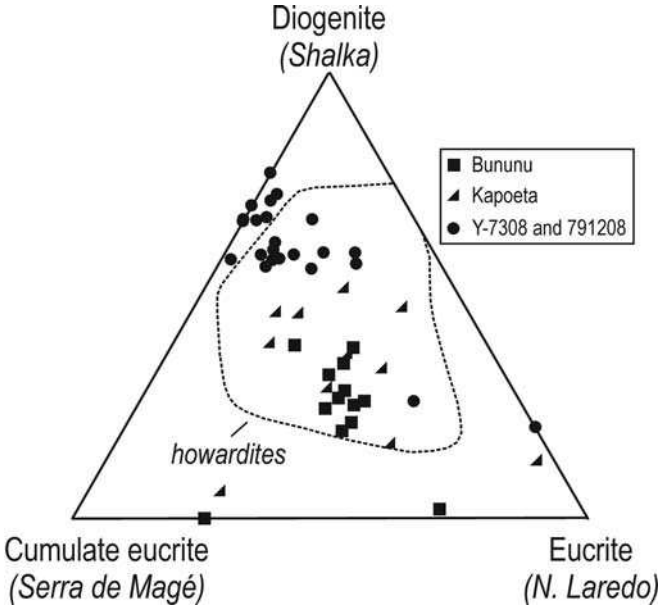

Fig. 13. Results of mixing calculations for the various low-K spherules and glassy fragments (Noonan 1974; Hewins and Klein 1978; Yagi et al. 1978; Klein and Hewins 1979; Noonan et al. 1980; Ikeda and Takeda 1984, and this study).

basaltic flows, but that more evolved and more K-rich lithologies than those actually known in the HED collection are exposed somewhere on Vesta. In this respect, our current sampling of the surface of Vesta (the HED) is necessarily incomplete. For example, cosmic-ray exposure ages for the HED suggest that all samples can be associated with one of only five impact events (Eugster and Michel 1995; Welten et al. 1997). In other words, only five localities at the surface of Vesta have been sampled, a number probably not sufficient to describe the geological diversity of the entire surface of the body. In September 2007, the Dawn spacecraft was launched to the asteroid belt and will begin studying Vesta and Ceres in 2011 (Russell et al. 2007). The planned remote sensing studies should allow the identification of chemically different areas on Vesta, and may help pinpoint the source regions of the K-rich impact glasses.

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